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(54) **Utilisation dans et pour la fabrication de compositions cosmétiques ou dermatologiques de polycondensats séquencés polyuréthanes et/ou polyurées à greffons siliconés**

Verwendung in und für die Herstellung von kosmetischen oder dermatologischen Zusammensetzungen von Blockpolykondensaten aus Polyurethanen und/oder Polyharnstoffen mit Silikon-Pfropfungen

Use in and for the preparation of cosmetic or dermatological compositions from polyurethane and/or polyurea blockpolycondensates having silicone grafts

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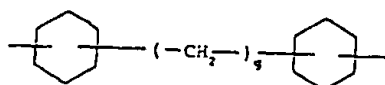
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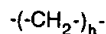
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(56) Documents cités:
EP-A- 0 277 816 **EP-A- 0 324 946**
EP-A- 0 636 361 **FR-A- 2 645 156**

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oder

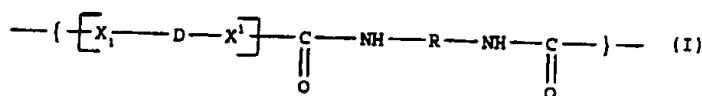


worin g eine ganze Zahl im Bereich von Null bis 3 und h eine ganze Zahl im Bereich von 1 bis 20 und vorzugsweise 2 bis 12 bedeutet.

44. Verfahren zur Herstellung eines Pseudo-Latex, dadurch gekennzeichnet, daß ein multisequentielles Polykondensat verwendet wird, dessen Kette aus wiederkehrenden Einheiten mindestens eines Blocks $\text{---}[\text{M}] \text{---}$ und mindestens eines Polyurethan- und/oder Polyharnstoffblocks $\text{---}[\text{N}] \text{---}$ und/oder $\text{---}[\text{G}] \text{---}$ mit in Kationen oder Anionen umwandelbaren Blöcken nach einem der Ansprüche 34 bis 43 verwendet wird, daß die in Kationen oder Anionen umwandelbaren Gruppen vollständig oder teilweise in einem organischen Lösungsmittel oder einem Gemisch von organischen Lösungsmitteln, die einen Siedepunkt unter dem Siedepunkt von Wasser aufweisen und mit Wasser mischbar oder teilweise mischbar sind, neutralisiert werden, die so hergestellte Lösung in einer wäßrigen Lösung dispergiert wird und das oder die organischen Lösungsmittel entfernt werden.
45. Verfahren nach Anspruch 44, dadurch gekennzeichnet, daß der Neutralisationsgrad im Bereich von 10 bis 100 % und vorzugsweise von 20 bis 100 % liegt.
46. Pseudo-Latex, der nach dem Verfahren des Anspruchs 44 oder 45 herstellbar ist.

Claims

- Use in and for the production of a cosmetic or dermatological composition of a polyurethane and/or polyurea block polycondensation product comprising a chain formed by the repetition of at least one polyurethane and/or polyurea block $\text{---}[\text{M}] \text{---}$ containing a polysiloxane graft.
- Use according to Claim 1, characterized in that the polycondensation product is multiblock and in that the chain is also formed by the repetition of a polyurethane and/or polyurea block $\text{---}[\text{N}] \text{---}$ containing nonionic and/or ionic groups and/or a polyurethane and/or polyurea block $\text{---}[\text{G}] \text{---}$ containing oligomers of organic polymers of average molecular weight, measured at the top of the GPC peak, of between 300 and 70,000 and/or a polysiloxane block $\text{---}[\text{L}] \text{---}$.
- Use according to either of Claims 1 and 2, characterized in that the polysiloxane-grafted polyurethane and/or polyurea block $\text{---}[\text{M}] \text{---}$ is of the following general formula:



in which:

X_1 represents, separately or jointly, ---O--- or ---NH--- ;

D represents a segment:



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Z is a trivalent hydrocarbon radical which may contain one or more heteroatoms;

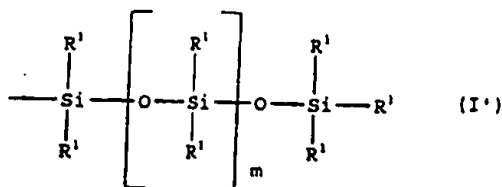
Q is a polysiloxane segment;

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R is a divalent radical chosen from the alkylene radicals of aliphatic, cycloaliphatic or aromatic type.

4. Use according to Claim 3, characterized in that the said segment Q is of the following general formula (I'):

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in which the radicals R¹, which are identical or different, are chosen from, on the one hand, C₁-C₂₀ monovalent hydrocarbon, haloalkyl or perhalogenated radicals which are free from ethylenic unsaturation, and, on the other hand, aromatic radicals, and m is an integer such that the average molecular weight, measured at the top of the GPC peak of the polysiloxane segment, is between 300 and 50,000.

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5. Use according to Claim 4, characterized in that the radicals R¹ are chosen from alkyl radicals, cycloalkyl radicals, aryl radicals and arylalkyl radicals.

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6. Use according to any one of Claims 3 to 5, characterized in that the trivalent radical Z is chosen from the radicals

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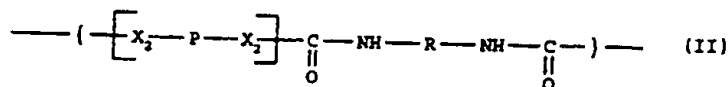


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in which a represents an integer ranging from 1 to 10.

7. Use according to any one of Claims 2 to 6, characterized in that the chain comprises the repetition of polysiloxane blocks [-L-] of the following general formula (II):

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in which:

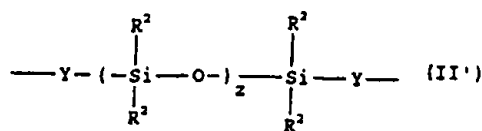
P is a polysiloxane segment,

X₂ represents, separately or jointly, -O- or -NH-, and

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R has the same meaning as indicated in Claim 3.

8. Use according to Claim 7, characterized in that the polysiloxane segment P has the general formula:



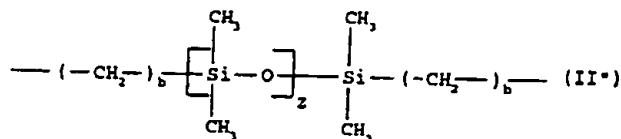
in which:

Y is a divalent hydrocarbon radical which may contain one or more heteroatoms;

R² has the same meanings as R¹ indicated in Claims 4 and 5;

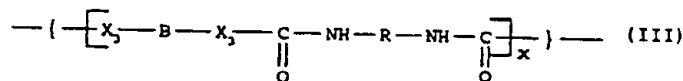
z is an integer which is such that the average molecular weight, measured at the top of the GPC peak of the polysiloxane segment, is between 300 and 50,000.

9. Use according to Claim 8, characterized in that the polysiloxane P is of the following formula:



in which b represents an integer ranging from 1 to 10 and z is an integer which is such that the average molecular weight, measured at the top of the GPC peak of the polysiloxane segment, is between 300 and 50,000.

10. Use according to any one of Claims 1 to 9, characterized in that the chain is formed by the repetition of a polyurethane and/or polyurea block ---[N-] of the following general formula (III):



in which:

X₃ represents, separately or jointly, ---O--- or ---NH--- ;

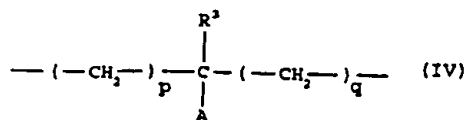
R has the same meaning as indicated in Claim 3;

x is an integer ranging from 1 to 10;

the radicals B, which are identical or different, are divalent hydrocarbon radicals which are nonionic or carry a positive or negative ionic charge.

11. Use according to Claim 10, characterized in that the said radical B carries a group or groups having one or more carboxylic functions and/or one or more sulphonic functions, the said carboxylic and/or sulphonic functions being partially or totally neutralized by an inorganic or organic base.

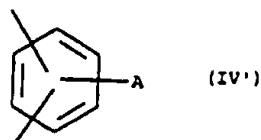
12. Use according to Claim 11, characterized in that the radical B is of the formula (IV):



in which R³ represents a linear or branched C₁-C₃ alkyl radical, A represents a carboxylic acid function (---COOH)

or sulphonic acid function ($-\text{SO}_3\text{H}$) or a salt of the said acid functions, and p and q, which can be identical or different, represent integers ranging from 1 to 5.

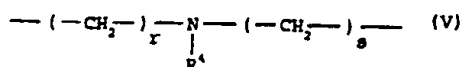
13. Use according to Claim 12, characterized in that the radical B is of the formula (IV):



in which A has the above meaning.

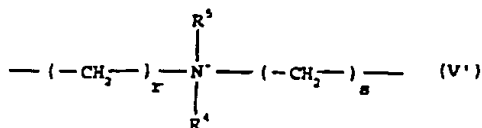
14. Use according to Claim 10, characterized in that the said radical B carries tertiary amine groups, the said tertiary amines being, partially or totally, either neutralized by an inorganic or organic base or quaternized, or else betainized.

15. Use according to Claim 14, characterized in that the radical B is of the following formula (V):



in which R^4 represents a linear or branched $\text{C}_1\text{--C}_4$ alkyl radical and r and s are two identical or different integers which may be between 1 and 10.

16. Use according to Claim 15, characterized in that, in neutralized, quaternized or betainized form, the radical B is of the following formula (V'):

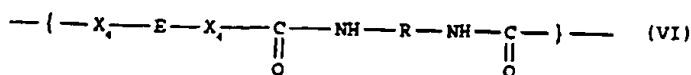


in which formula R^4 has the above meaning and R^5 represents either hydrogen (neutralization) or a linear or branched $\text{C}_1\text{--C}_{10}$ alkyl radical or an aromatic ring (quaternization), or a linear or branched $\text{C}_1\text{--C}_{10}$ alkyl radical which carries a carboxylate or sulphonate group (betainization).

17. Use according to Claim 10, characterized in that the said radical B carries nonionic groups chosen from the units provided by α,ω -diols, α,ω -diamines and aliphatic, cycloaliphatic or aromatic alcohol-amines.

18. Use according to any one of Claims 10 to 18, characterized in that the polycondensation product comprises blocks $[-\text{N}-]$ in which there is a nonionic segment B and blocks $[-\text{N}-]$ in which there is a cationic or anionic segment B.

19. Use according to any one of Claims 1 to 18, characterized in that the chain is formed by the repetition of a polyurethane and/or polyurea block $[-\text{G}-]$ containing oligomers of organic polymer, of the following formula:



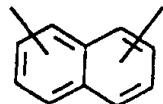
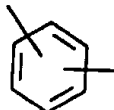
in which :

X_4 represents, separately or jointly, -O- or -NH-;

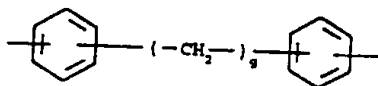
R has the same meaning as indicated in Claim 3;

E is an oligomer of an organic polymer chosen from polyethers, polyesters, polyester amides and polyamides, of average molecular weight, measured at the top of the GPC peak, of between 300 and 70,000, which can contain grafts on the chain or segments in the chain which carry a positive or negative ionic charge.

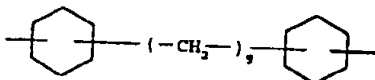
20. Use according to any one of Claims 3 to 19, characterized in that the radical R is chosen from the radicals of the following formulae:



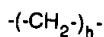
or



or



or



in which g is an integer between 0 and 3, and h is an integer between 1 and 20, preferably between 2 and 12.

21. Use in and for the production of a cosmetic or dermatological composition of a pseudo-latex which can be obtained by a preparation process which consists in using a multiblock polycondensation product whose chain is formed by the repetition of at least one block $\{-M-\}$ and at least one polyurethane and/or polyurea block $\{-N-\}$ and/or $\{-G-\}$ containing cationizable or anionizable groups, as is defined in any one of Claims 2 to 20, in partially or totally neutralizing the cationizable or anionizable groups in a solvent or a mixture of solvents which are organic having a boiling point less than that of water, and which are miscible or partially miscible with water; in dispersing the solution thus obtained in an aqueous solution; and then in removing the organic solvent or solvents.

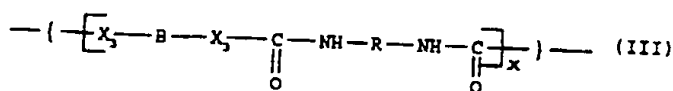
22. Use according to Claim 21, characterized in that the degree of neutralization varies from 10 to 100 % and preferably from 20 to 100 %.

23. Cosmetic or dermatological composition, characterized in that it contains in a cosmetically acceptable medium at least one block polycondensation product defined in accordance with any one of Claims 1 to 20.

24. Composition according to Claim 23, characterized in that it is provided in the form of a pseudo-latex as defined in either of Claims 21 and 22.

25. Composition according to Claim 23, characterized in that it is provided in the form of a solution of the polyurethane and/or polyurea block polycondensation product containing silicone grafts in an organic solvent; in the form of an "emulsion" or dispersion in water of a solution of the said polycondensation product in an organic solvent; or else in the form of an aqueous-organic solution of the said polycondensation product.
26. Composition according to any one of Claims 23 to 25, characterized in that it contains from 0.5 to 50 % by weight of polyurethane and/or polyurea block polycondensation product containing silicone grafts or of pseudo-latex as defined in Claim 24 relative to the total weight of the composition.
27. Composition according to any one of Claims 23 to 27, characterized in that it comprises additives chosen from fats, organic solvents, thickeners, emollients, antifoams, moisturizers, humectants, treatment agents, antiperspirants, alkali-forming agents, dyes, pigments, fragrances, preservatives, propellants, silicones and/or anionic, nonionic or amphoteric organic polymers which are compatible with polyurethanes or polyureas, and UV-A and/or UV-B sunscreens.
28. Product for the washing and/or care and/or treatment of hair, characterized in that it consists of a composition according to any one of Claims 23 to 27.
29. Make-up product, characterized in that it consists of a composition according to any one of Claims 23 to 27.
30. Skin care product, characterized in that it consists of a composition according to any one of Claims 23 to 27.
31. Use of a polycondensation product according to any one of Claims 1 to 20 as film-forming agent or as film-forming additive agent in a cosmetic or dermatological composition.
32. Use of a pseudo-latex according to either of Claims 21 and 22 as film-forming agent or as film-forming additive agent in a cosmetic or dermatological composition.
33. Method for the cosmetic treatment of keratinous materials, characterized in that it consists in applying to the said materials a composition according to any one of Claims 23 to 27.
34. Polyurethane and/or polyurea multiblock polycondensation product with polysiloxane grafts, characterized in that the chain is formed by the repetition of at least one polyurethane and/or polyurea block $[-M-]$ containing a polysiloxane graft, and also:

(i) by the repetition of a polyurethane and/or polyurea block $[-N-]$ of the following general formula (III):



in which:

X_3 represents, separately or jointly, $-\text{O}-$ or $-\text{NH}-$;

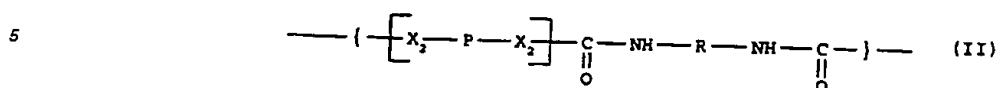
R is a divalent radical chosen from alkylene radicals of the aliphatic, cycloaliphatic or aromatic type;

x is an integer ranging from 1 to 10;

the radicals B, which are identical or different, can denote: (1) divalent hydrocarbon radicals which carry nonionic groups chosen from the units provided by the α , ω -diols; the α , ω -diamines and the aliphatic, cycloaliphatic or aromatic alcohol-amines; (2) divalent hydrocarbon radicals which carry anionic groups having one or more carboxylic functions and/or one of the sulphonic functions, the said carboxylic and/or sulphonic functions being partially or totally neutralized by an inorganic or organic base, (3) divalent hydrocarbon radicals which carry tertiary amine groups, the said tertiary amines being, partially or totally, either neutralized by an inorganic or organic base, or quaternized, or else betainized; and/or

(ii) by the repetition of a polyurethane and/or polyurea block $[-G-]$ containing oligomers of organic polymers of average molecular weight, measured at the top of the GPC peak, of between 300 and 70,000, and

(iii) by the repetition of a polysiloxane block $[-L-]$ of the following general formula (II):



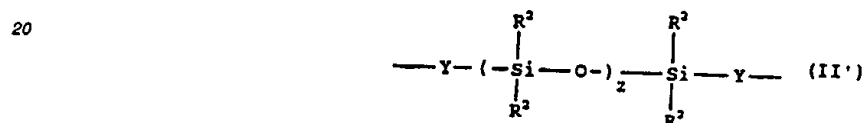
in which:

P is a polysiloxane segment,

X_2 represents, separately or jointly, $-\text{O}-$ or $-\text{NH}-$, and

R is a divalent radical chosen from the alkylene radicals of aliphatic, cycloaliphatic or aromatic type.

35. Polycondensation product according to Claim 34, characterized in that the polysiloxane segment P has the general formula:



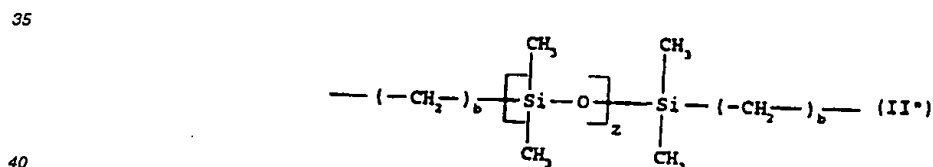
in which:

Y is a divalent hydrocarbon radical which may contain one or more heteroatoms;

R^2 has the same meanings as R^1 indicated in Claims 4 and 5;

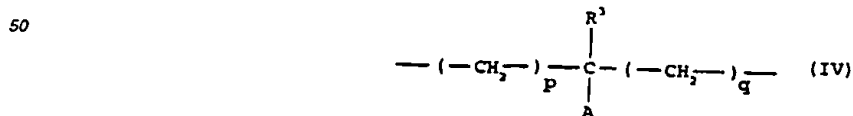
z is an integer which is such that the average molecular weight, measured at the top of the GPC peak of the polysiloxane segment, is between 300 and 50,000.

36. Polycondensation product according to Claim 35, characterized in that the polysiloxane P is of the following formula:



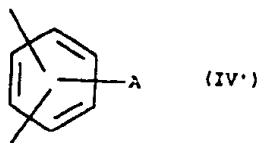
in which b represents an integer ranging from 1 to 10 and z is an integer which is such that the average molecular weight, measured at the top of the GPC peak of the polysiloxane segment, is between 300 and 50,000.

37. Polycondensation product according to Claim 34, characterized in that the radical B is of the formula (IV):



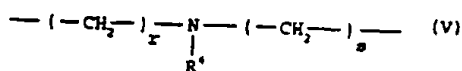
in which R^3 represents a linear or branched C_1 - C_3 alkyl radical, A represents a carboxylic acid function ($-\text{COOH}$) or sulphonic acid function ($-\text{SO}_3\text{H}$) or a salt of the said acid functions, and p and q, which can be identical or different, represent integers between 1 and 5.

38. Polycondensation product according to Claim 37, characterized in that the radical B is of the formula (IV'):



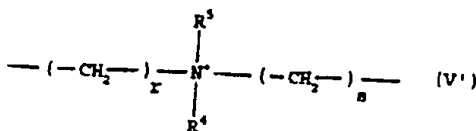
in which A has the above meaning.

39. Polycondensation product according to Claim 34, characterized in that the radical B is of the following formula (V):



25 in which R⁴ represents a linear or branched C₁-C₄ alkyl radical and r and s are two identical or different integers which may be between 1 and 10.

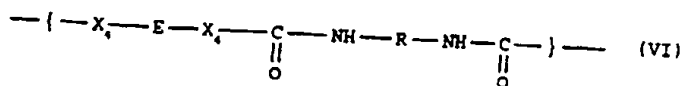
40. Polycondensation product according to Claim 34, characterized in that, in neutralized, quaternized or betainized form, the radical B is of the following formula (V'):



in which formula R⁴ has the above meaning and R⁵ represents either hydrogen (neutralization) or a linear or branched C₁-C₁₀ alkyl radical or an aromatic ring (quaternization), or a linear or branched C₁-C₁₀ alkyl radical which carries a carboxylate or sulphonate group (betainization).

41. Polycondensation product according to any one of Claims 34 to 40, characterized in that it comprises blocks $[-N-]$ in which there is a nonionic segment B and blocks $[-N-]$ in which there is a cationic or anionic segment B.

42. Polycondensation product according to any one of Claims 34 to 41, characterized in that the chain is formed by the repetition of a polyurethane and/or polyurea block $[-G-]$ containing oligomers of organic polymer, of the following formula:



in which:

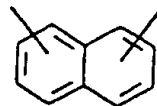
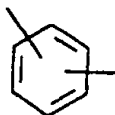
55 X⁴ represents, separately or jointly, -O- or -NH-;

R is a divalent radical chosen from alkylene radicals of aliphatic, cycloaliphatic or aromatic type;

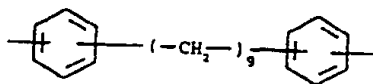
E is an oligomer of an organic polymer chosen from polyethers, polyesters, polyester amides and polyamides, of average molecular weight, measured at the top of the GPC peak, of between 300 and 70,000, which can

contain grafts on the chain or segments in the chain which carry a positive or negative ionic charge.

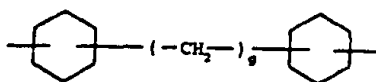
43. Polycondensation product according to any one of Claims 34 to 42, characterized in that the radical R is chosen from the radicals of the following formulae:



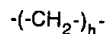
or



or



or



in which g is an integer between 0 and 3, and h is an integer between 1 and 20, preferably between 2 and 12.

44. Process for the preparation of a pseudo-latex, characterized in that a multiblock polycondensation product is used whose chain is formed by the repetition of at least one block $[-M-]$ and at least one polyurethane and/or polyurea block $[-N-]$ and/or $[-G-]$ containing cationizable or anionizable groups, as is defined in any one of Claims 34 to 43, in that the neutralization is carried out, partially or totally, of the cationizable or anionizable groups in an organic solvent or a mixture of organic solvents having a boiling point less than that of water, which are miscible or partially miscible with water; in that the solution thus obtained is dispersed in an aqueous solution; and then in that the organic solvent or solvents is or are removed.

45. Process according to Claim 44, characterized in that the degree of neutralization varies from 10 to 100 % and preferably from 20 to 100 %.

46. Pseudo-latex which can be obtained by the process of Claim 44 or 45.